Auger decay, Spin-exchange, and their connection to Bose-Einstein condensation of excitons in Cu_2O

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In view of the recent experiments of O'Hara *et al.* [1] on excitons in Cu_2O, we examine the interconversion between the angular-momentum triplet-state excitons and the angular-momentum singlet-state excitons by a spin-exchange process which has been overlooked in the past. We estimate the rate of this particle-conserving mechanism and find a substantially higher value than the Auger process considered so far. Based on this idea, we give a possible explanation of the recent experimental observations, and make certain predictions, with the most important being that the singlet-state excitons in Cu_2O is a very serious candidate for exhibiting the phenomenon of Bose-Einstein condensation.

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Bose-Einstein condensation [2] has been the subject of numerous theoretical and experimental studies. While in the recent years many of these studies have focused on the Bose-Einstein condensation of trapped alkali atoms [3], another possible candidate which can undergo this second-order phase transition is the exciton gas in semiconducting materials [4].

Excitons are much like positronium atoms. They are bound states which form between electrons and holes in a semiconductor, after the electrons get excited from the conduction band to the valence band, usually by some laser field. Since excitons consist of two fermions, in the limit where their separation is much larger than their Bohr radius, they are expected to behave like bosons. Many experiments have been performed with excitons in Cu_2O because of the many advantages of this material: It has a direct, but dipole-forbidden gap, which makes the lifetime of excitons rather long, it has isotropic effective electron and hole masses, it does not form bound states, biexcitons, or an electron-hole liquid, and finally the exciton binding energy is quite large.

The traditional way of observing the kinetic energy distribution of excitons is to look at the recombination spectrum, and more specifically the optical-phonon assisted lines. Since the optical phonons have a very weak dispersion relation and since the transition matrix element does not depend on the exciton momentum, the energy distribution of the emitted photons essentially gives the kinetic energy distribution of the excitons. Many experiments [5,6] have demonstrated that excitons do indeed obey Bose-Einstein statistics in the limit of high enough densities and low enough temperatures, with the luminescence spectrum fitting very accurately to Bose-Einstein distributions. This fitting procedure gives the temperature and the chemical potential of the gas, since these are essentially independent parameters. A crucial assumption underlying this procedure, is that very frequent collisions between the excitons bring the gas to a quasi equilibrium, with some time-dependent chemical potential and temperature, which in general differs from the lattice temperature that is kept very low, below 5 K. The typical effective temperature of the exciton gas is on the order of 10 up to 100 K. Knowing the temperature and the chemical potential, one can deduce the particle density, assuming an ideal Bose gas with an experimentally known total exciton mass. The densities turn out to be on the order of 10^{18} cm^{-3} from this method. Following this approach Snoke *et al.* [5,6] observed that the triplet-state (ortho)excitons do not Bose condense, but move along lines parallel and closely to the critical one, which are adiabats, i.e., along lines with constant entropy per particle. This effect has been examined theoretically in Ref. [8], and has been attributed to a competition between the acoustic-phonon cooling of the exciton gas, and an Auger heating mechanism which prevents the Bose-Einstein condensation of orthoexcitons. Lin and Wolfe have also reported in Ref. [7] this tendency of orthoexcitons to move along adiabats, but, most importantly, have observed evidence for the Bose-Einstein condensation of the angular-momentum singlet state (para)excitons [8].

However, recently O'Hara *et al.* have developed another method for estimating the density of the excitons [1]. By calibrating their photon detector, they have evaluated the number of photons that are being emitted, thus determining the number of orthoexcitons inside the crystal. They have also estimated the volume of the exciton gas by knowing the surface of the area of the laser light that creates the excitons, and with the assumption that the exciton gas has a typical depth inside the crystal, which is on the order of the absorption length of the laser light. Dividing the exciton number by the volume, they have found that the average density of the orthoexciton gas is two orders of magnitude smaller ($\sim 10^{16}$ cm^{-3}) than the one they estimate by the spectroscopic method. This implies that the gas should be completely classical, without showing any kind of quantum degeneracy.

Therefore one is confronted with a paradox, since from the one point of view the spectra can be fitted very ac-

curately to Bose-Einstein distributions, but on the other hand the densities seem to be quite lower than those one gets by this fit, and certainly much lower than the region where one would observe Bose statistics. Furthermore, Refs. [1,10,11] suggest that such low exciton densities might be due to a very effective Auger decay mechanism, where two excitons collide, the one recombines, transferring its energy to the other, which ionizes. The implication is that this Auger mechanism, which does not conserve the total number of excitons prevents the onset of Bose-Einstein condensation. Up to now the Auger process was thought to provide the only relatively fast channel for excitons to get destroyed [8]. However, in view of the very long intrinsic radiative lifetime of orthoexcitons reported recently in Refs. [1], the Auger decay rate should have a giant value, exceeding by three orders of magnitude the value calculated in Ref. [11].

In this study we examine another mechanism [13], in which two orthoexcitons with opposite J_z collide, where $\mathbf{J}$ is the total angular momentum of each exciton, exchanging their electrons or holes in the process, giving two paraexcitons in the final state. We make an estimate of the rate for this spin-exchange process, and find that it is rather high. Based on the result of our calculation, we propose that this ortho-to-para interconversion mechanism is actually the dominant one in the experimental conditions used so far. Strong experimental evidence that our argument is true provide Fig. 2 of the first paper in Refs. [1], Fig. 5 of the second paper in Refs. [1], and Fig. 4(a) of Ref. [7], where for late times it is clear that there is very slow decay of the paraexciton number. Consideration of this process removes the contradiction described above between the two methods that give the exciton density. An important conclusion drawn from this new scenario is that the Bose-Einstein condensation of paraexcitons is probable, since at late times they should form a cold and relatively dense gas. The spin-exchange mechanism, even if it converts one species into the other, conserves the total number of excitons. Since the orthoexcitons lie higher in energy than the paraexcitons due to the exchange interaction by an amount ΔE, the interconversion process also transfers energy to the exciton gas. We also note that our mechanism explains the observed sublinear dependence of the orthoexciton number [1] that is generated by the laser pulse as function of the laser power [14]. On the other hand, under extreme pumping conditions in the band-to-band region, we have a highly nonequilibrium system at early times and one can think that Auger processes between the free carriers are also effective.

Let us start by making an order of magnitude estimate of the decay rate $\Gamma_{o,p}$ of the ortho to paraexciton conversion process. We consider the process of two orthoexcitons with momenta $\mathbf{K}$ and $\mathbf{P}$ and opposite J_z colliding, giving two paraexcitons with momenta $\mathbf{K'}$ and $\mathbf{P'}$. Fermi's golden rule gives for the rate

$$\Gamma_{o,p} = \frac{2\pi}{\hbar} \sum_{\mathbf{K},\mathbf{P},\mathbf{K'},\mathbf{P'}} |M|^2 f^o_{\mathbf{K}} f^o_{\mathbf{P}} (1+f^p_{\mathbf{K'}})(1+f^p_{\mathbf{P'}}) \times \delta(E_{\mathbf{K'}} + E_{\mathbf{P'}} - E_{\mathbf{K}} - E_{\mathbf{P}} - 2\Delta E)\, \delta_{\mathbf{K}+\mathbf{P},\mathbf{K'}+\mathbf{P'}}, \quad (1)$$

where M is the matrix element for this process, $f^i_{\mathbf{K}}$ is the distribution function of the i species (ortho or para excitons), having a dispersion relation $E_{\mathbf{K}} = \hbar^2 K^2/2m$, with m being the total exciton mass. In this crude calculation we consider a cold ($\mathbf{K}, \mathbf{P} \approx 0$) orthoexciton gas, which allows us to write that

$$\Gamma_{o,p} \approx \frac{2\pi}{\hbar} N_o^2 \sum_{\mathbf{K'},\mathbf{P'}} |M|^2 (1+f^p_{\mathbf{K'}})(1+f^p_{\mathbf{P'}}) \times \delta(E^p_{\mathbf{K'}} + E^p_{\mathbf{P'}} - 2\Delta E)\, \delta_{\mathbf{K'}+\mathbf{P'},0}, \quad (2)$$

where N_i is the total number of excitons of species i. The energy conservation condition in the above equation implies that K' and P' are of order $(m\Delta E/\hbar^2)^{1/2}$. Since for these wavevectors the occupation number is much less than 1, we can ignore the enhancement factors $1 + f$ above. In addition, we argue below that the typical momentum exchange that enters the matrix element M is of order $a_B^{-1} \sim (mE_b/\hbar^2)^{1/2} \gg (m\Delta E/\hbar^2)^{1/2}$, where a_B is the exciton Bohr radius, and E_b is the exciton binding energy. Since $E_b \gg \Delta E$, M does not vary substantially in the sum of Eq. (2) and can be taken outside it,

$$\Gamma_{o,p} \approx \frac{2\pi}{\hbar} \frac{N_o^2}{2} |M|^2 \sum_{\mathbf{K'}} \delta(E^p_{\mathbf{K'}} - \Delta E). \quad (3)$$

The last sum is simply the density of states calculated for an energy ΔE. The interaction that enters the matrix element M is some screened Coulomb potential $V(q,\omega)$,

$$V(q,\omega) = \frac{4\pi e^2}{\Omega \epsilon(\mathbf{q},\omega) q^2}. \quad (4)$$

where Ω is the volume of the crystal, and $\epsilon(\mathbf{q},\omega)$ is the dielectric function [9]. The exciton wavefunction $\Phi_{\mathbf{K}}(\mathbf{r}_e - \mathbf{r}_h)$ of an exciton carrying momentum $\mathbf{K}$ can be written as

$$\Psi_{\mathbf{K}}(\mathbf{r}_e - \mathbf{r}_h) = \frac{1}{\sqrt{\Omega}} e^{i\mathbf{K}\cdot(\mathbf{r}_e+\mathbf{r}_h)/2} \sum_{\mathbf{q}} \phi_{\mathbf{q}}\, e^{i\mathbf{q}\cdot(\mathbf{r}_e-\mathbf{r}_h)}, \quad (5)$$

where $\mathbf{r}_e$ and $\mathbf{r}_h$ are the electron and hole coordinates, and $\phi_{\mathbf{q}} = 8(\pi a_B^3)^{1/2}/[1+(qa_B)^2]^2$ is the Fourier transform of the ground state hydrogenic wavefunction, $\Phi = e^{-r/a_B}/(\pi a_B^3)$, which we assume to be the relative electron-hole wavefunction. We have assumed that the two colliding orthoexcitons have $\mathbf{K} = \mathbf{P} = 0$; denoting the momenta of the electron and the hole in each pair as $\mathbf{k}, -\mathbf{k}$, and $\mathbf{p}, -\mathbf{p}$ [see Fig. 1], after the two excitons have exchanged their electrons or holes, and some momentum $\mathbf{q}$, conservation of energy and momentum requires that

$$\frac{\hbar^2(\mathbf{k}-\mathbf{p}+\mathbf{q})^2}{2m} = \Delta E. \quad (6)$$

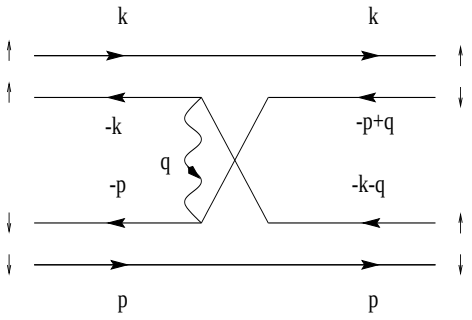

FIG. 1. The process of two orthoexcitons with opposite J_z colliding, exchanging their holes and some momentum $\mathbf{q}$, giving two paraexcitons in the final state. Time progresses from left to right. The straight lines with arrows pointing to the right (left) denote electrons (holes). The wiggly line denotes the Coulomb interaction. The arrows pointing upwards (downwards) denote $J_z = 1/2$ ($J_z = -1/2$) electrons or holes.

Since the exciton wavefunction has a momentum spread of order a_B^{-1}, we see that $p \sim k \sim a_B^{-1}$, or in other words, $\hbar^2 p^2/2m \sim E_b$. Because of the condition $\Delta E \ll E_b$, we conclude that q is also of order a_B^{-1} [15]. Furthermore, it is a rather good approximation to assume that $\epsilon(\mathbf{q},\omega) \approx \epsilon_0$ [9], the low-frequency dielectric constant of Cu_2O, which is approximately equal to 7.5, and thus

$$|M| \approx \frac{4\pi e^2 a_B^2}{\Omega \epsilon_0}. \tag{7}$$

After some trivial manipulations we can write for the rate of the orthoexciton conversion process $\Gamma_{o,p}/\Omega = n_o/\tau_{o,p}$, where n_i is the density of species i, and

$$\tau_{o,p}^{-1} \approx 16\pi\, n_o a_B^3 \sqrt{\frac{\Delta E}{E_b}}\, \frac{E_b}{\hbar}. \tag{8}$$

Let us now examine the reverse process of two paraexcitons colliding, giving two orthoexcitons. The energy scale which is very important for this process is the energy splitting ΔE between the orthoexcitons and paraexcitons in Cu_2O, which is equal to 12 meV [9] at the zone center, corresponding to a temperature of approximately 150 K. We can write for the decay rate $\Gamma_{p,o}/\Omega = n_p/\tau_{p,o}$, with

$$\tau_{p,o}^{-1} \approx \tau_{o,p}^{-1}\, (n_p/n_o)\, e^{-\Delta E/k_B T}, \tag{9}$$

where T is the temperature of the exciton gas. Thus, for temperatures which are much lower than $\Delta E/k_B$, the interconversion mechanism converts the orthoexcitons into paraexcitons, but not the reverse, since the para-ortho process is exponentially suppressed [$e^{-\Delta E/k_B T} \approx 0$]. On the other hand, for temperatures which are $\gtrsim \Delta E/k_B$, the two rates $\Gamma_{o,p}$ and $\Gamma_{p,o}$ can be comparable, depending on the relative densities of ortho and paraexcitons, and thus the net rate can be very low.

To calculate the actual value of the rate given by Eq. (8), we use the following numbers for excitons in Cu_2O (which have very low uncertainty): the binding energy is 153 meV, the energy splitting ΔE at the zone center is 12 meV, and finally the Bohr radius a_B is 5.3 Å, as given by a variational calculation presented in Ref. [9]. With these numbers we get

$$\tau_{o,p}^{-1} \approx 5 n_o (10^{16}\mathrm{cm}^{-3})\, \mathrm{ns}^{-1}, \tag{10}$$

where the notation $n(10^{16}\mathrm{cm}^{-3})$ means that the density is to be measured in units of $10^{16}\mathrm{cm}^{-3}$.

We can now compare the experimental decay rate of orthoexcitons that was measured recently by O'Hara *et al.* [1] with the above theoretical number on the one hand, and with the theoretical number for the Auger process on the other hand. For the low lattice temperature of ~ 2 K in this experiment, the average kinetic energy per particle of the gas of orthoexcitons is expected to be much less than ΔE, and thus we assume for the net interconversion rate $\Gamma_{o,p} - \Gamma_{p,o} \approx \Gamma_{o,p}$. The "two-body decay constant", $A \approx 10^{-16}$ cm^3/ns, that is extracted from the data given in Eq. (5) of the first paper in Refs. [1] has the same order of magnitude as the rate given by Eq. (10).

We mentioned before that the Auger process is expected theoretically to have a rather low decay rate, in view of the very long radiative lifetime of orthoexcitons which was reported recently in Refs. [1]. More specifically, in the theoretical study of the Auger process described in Ref. [11], a detailed analysis of this mechanism implied that the phonon-assisted Auger decay process was the dominant one. However, to get the rate, the authors used the orthoexciton radiative lifetime of 25 ns at a temperature of 10 K [16] that was measured in the past. In Refs. [1] the same quantity was measured to be approximately 10 μs, and since the radiative lifetime can be limited by imperfections or any other factor, the real radiative orthoexciton lifetime is at least 10 μs, or even longer. This implies that the phonon-assisted Auger decay rate, based on the theoretical study of Ref. [11] is negligible. These arguments provide strong evidence that the ortho to para exciton interconversion mechanism that we study here is really the dominant process.

We turn now to the contradiction between the two methods which have been used for determining the orthoexciton density. It is important to get first an estimate for the interparticle elastic scattering rates, in order to compare them with the rates of interconversion by spin-exchange. Typical scattering rates τ^{-1} for elastic collisions between excitons are expected to be on the order of $\tau^{-1} = n\sigma v_{\mathrm{th}}$, where σ is the scattering cross section, and v_{th} is the thermal velocity, $v_{\mathrm{th}} = (8k_B T/\pi m)^{1/2}$. At the low temperatures of interest one can assume hard-sphere scattering between the excitons. If a is the scattering length, then for identical bosons $\sigma = 8\pi a^2$. Recently the scattering length for excitons in Cu_2O has been calculated to be on the order of $2a_B$ [17] with use of Monte-Carlo simulations. Therefore we get

$$\tau^{-1} \approx 0.1\, n(10^{16}\mathrm{cm}^{-3})\, \sqrt{\mathrm{T(K)}}\, \mathrm{ns}^{-1}, \tag{11}$$

assuming that the total exciton mass is equal to 3 electron masses [9]. Here the density is measured in units of 10^{16} cm^{-3}, and the temperature in units of degrees Kelvin.

After the laser pulse starts to decrease, the paraexcitons become the dominant component of the gas because of the interconversion mechanism. For typical paraexciton densities of 10^{17} cm^{-3} and thermal velocities of order 50 K, one sees from Eq. (11) that the typical scattering times are of order 100 ps, and the paraexcitons should be able to establish thermal equilibrium. The paraexcitons should also have a well-defined chemical potential, since after the initial times that the orthoexcitons convert to paraexcitons due to the interconversion process, their number does not vary significantly with time. By contrast, the orthoexciton-orthoexciton elastic scattering processes become less and less frequent because of their decreasing density, even if the orthoexciton-paraexciton collisions can bring them to thermal equilibrium; we claim, however, that chemical equilibrium has not been established in the orthoexciton gas, since the orthoexcitons have a relatively fast way of converting into paraexcitons and their number is not conserved. One can speculate that under such circumstances the orthoexciton gas could have a chemical potential which is rather low, but this is a non-equilibrium problem, and it requires a detailed study. One, for example, could use the Boltzmann equation to describe all the important processes which take place, and derive the distribution function of the orthoexcitons as a function of time.

There are some remarks one can make concerning this model we are proposing. Firstly, the estimate we made for the interconversion rate, Eqs. (1) and (2), does not assume thermal equilibrium, which is rather important in our problem. Secondly the Bose-Einstein condensation of paraexcitons does not seem hard, since as we explained there is no efficient mechanism which would destroy them on the timescales of interest, and their expansion could be the only factor against them in order to Bose condense. However the expansion is not expected to be dramatic, and it can also be reduced by applying some stress to the crystal, thus effectively trapping the excitons.

Finally, it has been argued is Ref. [8], that the orthoexcitons – provided they are not far away from equilibrium – have to move along lines of constant entropy, along which $n_o \propto T^{3/2}$. To derive this result, the authors assumed that there is a competition between acoustic-phonon cooling and Auger heating. Since the phonon cooling rate is $\propto -T^{3/2}$ for low lattice temperatures, and the Auger heating rate is $\propto n_o$, $n_o \propto T^{3/2}$. Remarkably, if indeed the Auger process is negligible, and the interconversion process is the dominant mechanism, the heating rate due to this effect is equal to $\Delta E/\tau_{o,p}$, and thus still proportional to n_o. Since this argument does not depend on the quantum degeneracy of the gas, n_o should still be proportional to $T^{3/2}$: we conclude again that the orthoexcitons are expected to move parallel to the phase boundary, along adiabats, in contrast to the paraexcitons which most probably Bose condense. More experimental and theoretical work are required to verify these predictions.

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[13] This process has to be distinguished from the phonon-assisted ortho-to-para exciton interconversion mechanism, a process which has already been explored in Ref. [12] (see also Ref. [8]) and which does not depend on the particle density. We will not consider it further here, but it would certainly have to be taken into account in a complete quantitative study of the problem.

[14] We should stress out that the paraexcitons have only a very weak phonon-assisted line in the recombination spectrum (their direct recombination is highly forbidden [9]), which makes their observation impossible at early times, during the action of the laser pulse.

[15] In the limit $\Delta E \to 0$, $\mathbf{q} = \mathbf{p} - \mathbf{k}$, and then one needs to calculate the sum $\sum_{\mathbf{k},\mathbf{p}} |\phi_{\mathbf{k}}|^2 |\phi_{\mathbf{p}}|^2 / |\mathbf{k} - \mathbf{p}|^2$ to get M.

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